RL-TR-94-231 Final Technical Report December 1994



# HIGH T<sub>C</sub> SUPERCONDUCTOR/ FERROELECTRIC HETEROSTRUCTURES

**SRI** International

Dr. Daniel F. Ryder, Jr.



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

This effort was funded totally by the Laboratory Director's fund.

19950210 073

Rome Laboratory
Air Force Materiel Command
Griffiss Air Force Base, New York

This report has been reviewed by the Rome Laboratory Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RL-TR-94-231 has been reviewed and is approved for publication.

APPROVED:

MICHAEL J. SUSCAVAGE

Michael J. Buccovage

Project Engineer

FOR THE COMMANDER:

ROBERT V. McGAHAN

Acting Director

Electromagnetics & Reliability Directorate

Robert V. Mc Hahan

If your address has changed or if you wish to be removed from the Rome Laboratory mailing list, or if the addressee is no longer employed by your organization, please notify RL (  $^{\rm ERX}$  ) Hanscom AFB MA 01731. This will assist us in maintaining a current mailing list.

Do not return copies of this report unless contractual obligations or notices on a specific document require that it be returned.

# REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to everage 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other sepect of this collection of information, including suggestions for reducing this burden, to Weshington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Dayle Highway S. Jah 1904. Advances No. 2015.

Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0189), Weehington, DC 20503.					
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED			
	December 1994	Final			
4. TITLE AND SUBTITLE	5. FUNDING NUMBERS C - F30602-91-D-0001,				
HIGH T <sub>C</sub> SUPERCONDUCTOR/FERR	1 -				
6. AUTHOR(S)	PR - LDFP				
		TA - 04			
Dr. Daniel F. Ryder, Jr.	WU - P3				
7. PERFORMING ORGANIZATION NAME(S) SRI International	8. PERFORMING ORGANIZATION REPORT NUMBER				
333 Ravenswood Ave	N/A				
Menlo Park CA 94025		N/ 25			
9. SPONSORING/MONITORING AGENCY N. Rome Laboratory (ERX) 80 Scott Rd	10. SPONSORING/MONITORING AGENCY REPORT NUMBER				
Hanscom AFB MA 17031-2090	RL-TR-94-231				
11. SUPPLEMENTARY NOTES					
Rome Laboratory Project Engineer: Michael J. Suscavage/ERX/(617) 478-5252 This effort was funded totally by the Laboratory Director's fund.					
12a. DISTRIBUTION/AVAILABILITY STATEME	NT	12b. DISTRIBUTION CODE			
Approved for public release	e; distribution unlimit	ed.			
13. ABSTRACT (Maximum 200 words)					
و مینمیسا		mio (nom) described on			

Thin films of the ferroelectric perovskite, Ba  $Sr_1$   $TiO_3$  (BST), were deposited on superconducting  $(100)YBa_2Cu_3O_x(YBCO)/(100)Yttria-stabilized$  (YSZ) substrates and (100)Si by ion-beam sputtering. Microstructural and compositional features of the ceramic bilayer were assessed by a combination of x-ray diffraction (XRD) and scanning electron microscopy. The films were smooth and featureless, and energy dispersive x-ray spectroscopy (EDX) data indicated that film composition closely matched target composition. XRD analysis showed that films deposited on YBCO substrates were highly c-axis textured, while the films deposited on (100)Si did not exhibit any preferred growth morphology. The superconducting properties of the YBCO substrate layer were maintained throughout the processing stages and, as such, it was demonstrated that ion beam sputtering is a viable method for the deposition of Ferroelectric/YBCO heterostructures.

14. SUBJECT TERMS			15 NUMBER OF PAGES 12	
Ferroelectric, Supercon	1& PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

#### **ABSTRACT**

Thin films of the ferroelectric perovskite, Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (BST), were deposited on superconducting (100) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> (YBCO) / (100) Yttria-stabilized zirconia (YSZ) substrates and (100) Si by ion-beam sputtering. Microstructural and compositional features of the ceramic bilayer were assessed by a combination of x-ray diffraction (XRD) and scanning electron microscopy. The films were smooth and featureless, and energy dispersive x-ray spectroscopy (EDX) data indicated that film composition closely matched target composition. XRD analysis showed that films deposited on YBCO substrates to be highly c-axis textured, while the films deposited on (100) Si did not exhibit any preferred growth morphology. The superconducting properties of the YBCO substrate layer were maintained throughout the processing stages, and as such, it was demonstrated that ion beam sputtering is a viable method for the deposition of Ferroelectric/YBCO heterostructures.

#### **INTRODUCTION**

The research on thin film ferroelectric materials has been primarily driven, in recent times, by the development of the non-volatile ferroelectric random access memory (FRAM) device, and the reader is referred to the Reference literature list (particularly, the work of Ramesh et.al.) for details. In general, and similar to other applications of electronic ceramic thin films, the performance of FRAM devices is highly influenced by the crystalline quality of the ferrolectric film and the characteristics of the film-electrode interface. By utilizing a substrate (i.e., bottom electrode) which is both lattice and chemically matched, it should be possible to induce epitaxial growth of the ferroelectric layer and thus minimize defect structures associated with grain boundary effects. The perovskite ferroelectrics (e.g., (Ba,Sr)TiO<sub>3</sub>, Pb(Zr,Ti)O<sub>3</sub>, etc.) and the perovskite YBCO superconductor possess similar lattice structure (i.e., 2-3% lattice match in the a-b plane) and crystal chemistry and thus provide an ideal system from which to base an experimental program. While the work of Ramesh et.al. at Bellcore has demonstrated that important ferroelectric performance properties (i.e., fatigue and ageing) of pulsed laser-deposited Pb(Zr,Ti)O3 were improved when the films were grown heteroepitaxially on YBCO, they did not comment on the superconducting properties of the YBCO electrode. An objective of this work was to investigate how the superconducting properties of the YBCO layer was effected by the deposition processing of the BST layer.

#### **EXPERIMENTAL**

Thin Film Processing

 $Ba_xSr_{1-x}TiO_3$  (x = 0.25, 0.75) films were ion beam sputter deposited from stoichiometric ceramic oxide targets. A 3 cm Kaufman source (Commonwealth Scientific, Inc.) was utilized to generate the Ar+ ion sputter beam which was positioned at an incident angle of 45° to the target. A low energy, gridless ion source (Commonwealth Scientific, Inc.), which was directed at the substrate with an incident angle of 45°, was utilized to preclean (by Ar+ ion sputtering) the substrates prior to film deposition. A gas dispersion ring located near the substrate was used to introduce oxygen during deposition. Films were deposited at a total pressure of 2.0 x 10<sup>-4</sup> torr (1.0 x 10<sup>-4</sup> torr Ar and 1.0 x 10<sup>-4</sup> torr  $O_2$ ). Substrate temperature was varied within the range of 550 to 650 °C over the course of this study. Deposition rate was on the order of 0.3 to 0.6 nm/min., and final film thickness was on the order of 200 to 250 nm as measured by surface profilometry.

The YBCO/YSZ substrates were commercially obtained (Excel Superconductor, Bohemia, NY) and were used as is. The silicon substrates were briefly etched in 10% aqueous HF and rinsed in distilled, deionized H<sub>2</sub>O prior to entry to the vacuum system. Given that the principal study related to film deposition on YBCO and that the Si substrate depositions were only done for comparison purposes, it is noted that the film deposition conditions would in all likelihood result in the formation of an SiO<sub>2</sub> layer on the Si which would negatively impact the quality of the BST/Si film samples. Prior to film deposition, the substrates were heated to the deposition temperature and sputter cleaned (i.e., removal of approximately a 10 nm surface layer) by a lowenergy Ar+ ion beam.

#### **RESULTS and DISCUSSION**

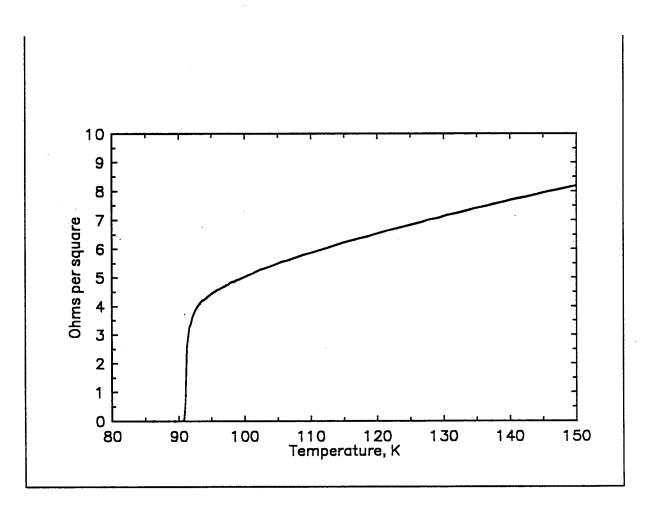
BST films deposited *in situ* at a substrate temperature of approximately 650 °C were visually observed to be smooth and optically reflective. Electrical measurements showed that the resistivity of the crystalline BST films ranged from  $10^4$  to  $10^8$   $\Omega$ -cm, with the more resistive films associated with higher deposition temperatures. Bulk sample data reported in the literature indicate a resistivity on the order of  $10^9$  to  $10^{10}$   $\Omega$ -cm and as such, it is presumed that low level impurities (not detected by EDX measurements) and/or defect structures (i.e., oxygen vacancies) reduced film resistivities. Due to the high leakage current of the deposited films, the ferrolelctric properties of a test Pt/BST/YBCO capacitor structure could not be analyzed.

XRD analysis indicated that films deposited on (100) YBCO were highly c-axis oriented, while films deposited on (100) Si did not exhibit any preferred orientation effect. This is

consistent with our previous results relating to the sol-gel processing of  $Pb(Zr,Ti)O_3$  films on (100) YBCO and Pt-coated Si, but the microstructural quality of the sputtered films were superior to that of the sol-gel-derived films.

The superconducting properties of the YBCO base layer were determined by the DC four probe method both prior and after deposition of the BST overlayer. Figure 1 shows that *in situ* BST film processing had minimal effect on the electrical properties of the YBCO layer as a





sharply-defined T<sub>c</sub> of approximately 90 K is maintained.

#### **CONCLUSIONS**

Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (x=0.25, 0.75) films were deposited *in situ* on (100) YBCO/YSZ substrates by ion beam sputtering. Based on EDX results, and substantiated by the analysis of XRD data, the composition of a deposited film was consistent with the stoichiometry of the single oxide target utilized. XRD analysis showed that films deposited on "lattice-matched" YBCO substrates to be highly c-axis textured, while films deposited at the same growth conditions on (100) Si did not exhibit any preferred crystallographic orientation. The resistivity of the ion-beam sputtered BST films were lower that bulk reported values and is probably related to low level impurities and/or oxygen defects. The superconducting properties of the YBCO base layer were not effected by the BST deposition process, and as such ion beam sputtering affords a viable method for the fabrication of Ferroelectric/Superconductor -based device structures.

#### REFERENCES

- C.S. Chern, S. Liang, Z.Q. Shi, S. Yoon, A. Safari, P. Lu, and B.H. Kear, "Epitaxial Growth of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> Thin Films on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Electrodes by PE-MOCVD" in <u>Metal-Organic Chemical Vapor Deposition of Electronic Ceramics</u>, Mat. Res. Soc. Symp. Proc., S.D. Desu, D.B. Beach, B.W. Wessels, and S. Gokoglu, Eds., Vol. **335**, 29, (1994).
- S.R. Gilbert, B.W. Wessels, D.A. Neumayer, T.J. Marks, J.L. Schindler, and C.R. Kannewurf, "Preparation of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> Thin Films by Metalorganic Chemical Vapor Deposition and Their Properties", in Metalorganic Chemical Vapor Deposition of Electronic Ceramics, Mat. Res. Soc. Symp. Proc.,
- S.D. Desu, D.B. Beach, B.W. Wessels, and S. Gokoglu, Eds., Vol. 335, 41, (1994).
- D.L. Kaiser, M.D. Vaudin, G. Gillen, C-S. Hwang, L.H. Robins, and L.D. Rotter, "Growth of BaTiO<sub>3</sub> Thin Films by MOCVD", in <u>Metal-Organic Chemical Vapor Deposition of Electronic Ceramics</u>, *Mat. Res. Soc. Symp. Proc.*, S.D. Desu, D.B. Beach, B.W. Wessels, and S. Gokoglu, Eds., Vol. 335, 47, (1994).
- R. Ramesh, W.K. Chan, H. Gilchrist, B. Wilkens, T. Sands, J.M. Tarascon, V.G. Keramidas, J.T. Evans, Jr., F.D. Gealy, and D.K. Fork, "Oxide Ferroelectric / Cuprate Superconductor Heterostructures: Growth and Properties", in Ferroelectric Thin Films II, Mat. Res. Soc. Symp. Proc., A.I. Kingon, E.R. Meyers, and B. Tuttle, Eds., Vol. 243, 477, (1991).
- R. Ramesh, W.K. Chan, B. Wilkens, T. Sands, J.M. Tarascon, V.G. Keramidas, and J.T. Evans, "Fatigue and Aging in Ferroelectric PbZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> / YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Heterostructures", *Integrated Ferroelectrics*, 1(1), 1, (1992).

# **MISSION**

## **OF**

### ROME LABORATORY

Mission. The mission of Rome Laboratory is to advance the science and technologies of command, control, communications and intelligence and to transition them into systems to meet customer needs. To achieve this, Rome Lab:

- a. Conducts vigorous research, development and test programs in all applicable technologies;
- b. Transitions technology to current and future systems to improve operational capability, readiness, and supportability;
- c. Provides a full range of technical support to Air Force Materiel Command product centers and other Air Force organizations;
  - d. Promotes transfer of technology to the private sector;
- e. Maintains leading edge technological expertise in the areas of surveillance, communications, command and control, intelligence, reliability science, electro-magnetic technology, photonics, signal processing, and computational science.

The thrust areas of technical competence include: Surveillance, Communications, Command and Control, Intelligence, Signal Processing, Computer Science and Technology, Electromagnetic Technology, Photonics and Reliability Sciences.